

# PATENT SPECIFICATION

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749,479



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## COMPLETE SPECIFICATION

### New Polyamides

5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new polyamides and more particularly to new polyamides which are well adapted for use in conventional plastic shaping equipment such as extrusion or injection moulding equipment.

15 Polyamides have been proposed heretofore from one or more of a variety of diamines and dicarboxylic acids and/or aminocarboxylic acids or from amide-forming derivatives of these materials, but all of the heretofore known polyamides have properties which have tended 20 to prevent or minimise their usage for moulding from conventional injection moulding equipment and other plastic shaping operations. In particular, the known polyamides, at temperatures just above their melting points, 25 are too fluid for handling easily in such equipment.

30 We have now found that the incorporation of a small amount of bis-hexamethylenetriamine or an amide-forming derivative thereof into a polyamide-forming composition has the effect of modifying the resulting polyamide in such a way that melts of the modified polyamides remain highly viscous over a relatively wide range of temperature above their melting 35 points and are well suited for handling in conventional plastic shaping equipment.

40 Also we have found the modification effected in this way is not accompanied by any serious change in the otherwise excellent properties of the polyamides for moulding and the like purposes.

According to the present invention we provide new polyamides formed from a composition

45 comprising one or more diamines and one or more dicarboxylic acids, in essentially equimolecular proportions, and, optionally, an aminocarboxylic acid, as such or in the form of amide-forming derivatives thereof, characterised in that the said composition also 50 contains a small amount of bis-hexamethylenetriamine or an amide-forming derivative thereof, together with an equivalent proportion of dicarboxylic acid.

55 A process for the manufacture of said new polyamides comprises heating the polyamide-forming composition of the kind described above at least until filaments formed from a melt of the polyamide can be extended by cold-drawing into fibres.

60 Amide-forming derivatives of the ingredients include esters or the amides of the acids and the preformed salts of the acids with the diamines. It is preferred to use the ingredients in the form of the preformed salts thereof, since these salts are easily obtained in a pure 65 form and since they contain the respective ingredients in equivalent proportions. With bis-hexamethylene triamine and adipic acid, however, the salt is not easily isolated and may 70 therefore be used in aqueous solution.

75 A small proportion of a mono-functional amide-forming reactant, for example acetic acid, may also be used for the purpose of stopping the polyamide-forming reaction at any desired stage in the manner described in Specification No. 495,790.

80 A small proportion of a delustrant, pigment or other colouring material, for example, titanium dioxide, may be included among the ingredients, or added at any stage in the process.

85 The amount of bis-hexamethylene triamine that is used as such or in the form of an amide-forming derivative, is necessarily small since the use of a large amount results in the production of an intractable material, insoluble

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in the normal polyamide solvents and which is unsuitable for moulding. In general, the amount used is from 0.3 to 3.18 molar per cent of the total diamine and aminocarboxylic acid content of the polyamide-forming composition. If less than 0.3% is used the effect on the properties of the polyamide is still apparent but is so diminished as not to be of technical value. Within this broad range, variations need to be made according to the amount of mono-functional amide-forming reactant used. Thus in absence of such a reactant the preferred molar per cent is from 0.3 to 1.05. With the use of 0.5 molar per cent of acetic acid calculated on the total diamine and aminocarboxylic acid content, the preferred molar per cent of bis-hexamethylene triamine is from 0.6 to 1.8; with 1.4 molar per cent of acetic acid it is 1.2 to 3.18. More than 1.4 molar per cent of acetic acid is not generally used. The preferred proportions to correspond with any desired proportions of mono-functional reactant can be readily determined by trial. The preferred proportions of bis-hexamethylene triamine can be reduced, also, by subjecting the polyamide during manufacture to vacuum treatment or by passing an inert gas through the melt, as is illustrated in the Examples.

The heating of the polyamide-forming composition is carried out in accordance with conventional practice for the manufacture of fibre-forming polyamides, usually at temperatures from about 265–285° C. The heating is carried out under conditions which permit the removal of water or other by-product, at least during the later stages of the heating. Reduced pressures may be used to facilitate the removal of water or other by-product and a stream of any oxygen-free gas, for example, nitrogen, may be passed through and/or over the reaction mass.

Although the new polyamides have excellent fibre-forming properties, they find their greatest utility in the art as materials for plastic shaping, as by extrusion or by injection moulding.

According therefore to a further feature of the invention we provide a process for producing shaped polyamide articles by means of conventional plastic shaping equipment wherein there are used the polyamides of this invention.

The invention is illustrated but not limited by the following Examples in which parts and percentages are expressed by weight.

#### EXAMPLE 1.

A mixture of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and sebacic acid, and 0.3 part of the neutral salt formed in aqueous solution from bis-hexamethylene triamine and adipic acid is heated at 220° C. for 2 hours in a closed vessel which has been previously purged out with oxygen-free nitrogen, and evacuated

to a pressure of 10–15 mm. of mercury. The vessel and contents are allowed to cool, the vessel is opened, fitted with means for passing oxygen-free nitrogen through the contents, again purged out with oxygen-free nitrogen, and the heating is continued until the polymer is again fully molten, and thereafter for 1½ hours at 282° C. at atmospheric pressure, whilst a slow stream of oxygen-free nitrogen is passed through the melt. The vessel and contents are allowed to cool when the product is obtained as a tough, white solid of inherent viscosity (1% solution in *m*-cresol) 1.09.

#### EXAMPLE 2.

A mixture of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and adipic acid and 0.75 part of the neutral salt formed in aqueous solution from bis-hexamethylene triamine and adipic acid is formed into a polymer in the manner of Example 1 except that the heating at atmospheric pressure is for 20 minutes instead of 1½ hours. The product is a tough, white solid, inherent viscosity (1% solution in *m*-cresol) 1.2.

#### EXAMPLE 3.

A solution of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and 4 parts of the neutral salt of bis-hexamethylene triamine and adipic acid in 66 parts of distilled water, together with 0.23 part of acetic acid, is heated for 1.5 hours at 250 lbs. per square inch pressure in a vessel which has been purged out with oxygen-free nitrogen, the temperature being raised during this period from 215° C. to 240° C. The pressure is gradually reduced over a further 1½ hours to atmospheric pressure at which pressure the melt temperature is maintained for 1 hour.

The polymer is extruded from the vessel under 30 lb./sq. inch of oxygen-free nitrogen and quenched. The product is a tough, white solid which has a softening point of 268° C. The polyamide is not completely soluble in the solvents used for the determination of intrinsic viscosity.

#### EXAMPLE 4.

A solution of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and adipic acid and 2.5 parts of the neutral salt of bis-hexamethylene triamine and adipic acid in 66 parts of distilled water together with 0.23 part of acetic acid is polymerised as in Example 3.

The product is a tough, white product which has a softening point of 266° C. and an intrinsic viscosity in 90% formic acid of 1.390.

In order to demonstrate the utility of the new polyamides for injection moulding, samples were tested in the apparatus hereinafter described.

The apparatus consists of a cylinder of ¾" diameter 4" in length, fitted at the base with a die, the hole in the die being 0.052" in

5 diameter. The cylinder is surrounded by a heating element, lagged to prevent heat loss and means for adjusting and recording the temperature. Fitting into the cylinder is a piston at the upper extremity of which there is a weight of 12½ lbs.

10 In carrying out the tests, a quantity of the polyamide is dried at 110° C. for 4 hours in a stream of oxygen-free nitrogen at a pressure of 2 mms. of mercury and is then placed in the cylinder, the temperature of the cylinder is brought up to a temperature just above the softening point of the polyamide, and the temperature is maintained for 10 minutes.

15 The piston is then placed in the cylinder, whereupon the softened polyamide is forced through the hole in the die by virtue of the

pressure exerted upon the uppermost surface of the polyamide.

20 Thereafter, the temperature is increased slowly, and at a series of increasing temperatures, measurements are made of the quantities of molten polyamide extracted from the hole in the die. A record is made of the lowest temperature at which extrusion commences and the lowest temperature at which the polyamide under test is extruded from the hole at the rate of 0.5 gram per minute.

25 The results obtained are expressed in the following Table, and, for comparative purposes, data are also given for corresponding polyamides which have not been modified with the bis-hexamethylene triamine.

1

	Lowest Temperature at which extrusion commences °C.	Lowest Temperature at which product is extruded at 0.5 g./min.	Difference °C.
Polyamide from hexamethylene diamine and adipic acid	266	267	1
Product of Example 1	235	255	20
Product of Example 2	270	314	44
Product of Example 3	269	331	62
Product of Example 4	274	285	11

35 The results expressed in the Table indicate that, whereas the unmodified polyamides are extruded inconveniently rapidly at temperatures above their melting points, the modified polyamides may be extruded much more slowly over a wider range of temperatures.

40 In order to indicate that there has been no

serious falling off of other physical properties of the unmodified polyamides films of thickness 0.004—0.008" were made up by pressing melts, and physical measurements were made from samples of these films. The average results obtained are expressed in the following Table:—

45

Property	Polyamide from hexamethylene diamine and adipic acid	Product of Example 1	Product of Example 2	Product of Example 3	Product of Example 4
Tensile strength in lb. per square inch	6370	5240	7300	5860	5467
Elongation at break as %	57	290	250	200	35
Modulus at 10% in lb. per square inch	6320	3050	3380	4300	4540
Permanent set as %	37	173	162	88	12

What we claim is:—

- 1) New polyamides formed from a composition comprising one or more diamines and one or more dicarboxylic acids, in essentially equimolecular proportions, and, optionally, in aminocarboxylic acid, as such or in the form of amide-forming derivatives thereof, characterised in that the said composition also contains a small amount of bis-hexamethylenetriamine or an amide-forming derivative thereof, together with an equivalent proportion of dicarboxylic acid.
- 2) New polyamides as claimed in claim 1 wherein the amount of bis-hexamethylene-

triamine or amide-forming derivative thereof is from 0.3 to 3.18 molar per cent of the total diamine and aminocarboxylic acid content of the polyamide-forming composition.

- 3) New polyamides as hereinbefore particularly described and ascertained especially with reference to the foregoing Examples.

- 4) Process for producing shaped polyamide articles by means of conventional plastic shaping equipment wherein there are used the polyamides claimed in any of the preceding claims.

ALFRED O. BALL,  
Agent for the Applicants.

#### PROVISIONAL SPECIFICATION

#### New Polyamides

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This invention relates to new polyamides and more particularly to new polyamides which are well adapted for use in conventional plastic shaping equipment such as extrusion or injection moulding equipment.

Polyamides have been proposed heretofore from one or more of a variety of diamines and dicarboxylic acids and/or aminocarboxylic acids or from amide-forming derivatives of

these materials, but all of the heretofore known polyamides have properties which have tended to prevent or minimise their usage for moulding from conventional injection moulding equipment and other plastic shaping operations. In particular, the known polyamides, at temperatures just above their melting points, are too fluid for handling easily in such equipment.

We have now found that the incorporation of a small amount of bis-hexamethylenetriamine or an amide-forming derivative thereof into a polyamide-forming composition has the effect of modifying the resulting poly-

amide in such a way that melts of the modified polyamides remain highly viscous over a relatively wide range of temperature above their melting points and are well suited for handling in conventional plastic shaping equipment.

Also we have found the modification effected in this way is not accompanied by any serious change in the otherwise excellent properties of the polyamides for moulding and the like purposes.

According to the present invention we provide new polyamides formed from a composition comprising one or more diamines and one or more dicarboxylic acids, in essentially equimolecular proportions, and, optionally, an aminocarboxylic acid, as such or in the form of amide-forming derivatives thereof, characterised in that the said composition also contains a small amount of bis-hexamethylene triamine or an amide-forming derivative thereof, together with a corresponding essentially equivalent proportion of dicarboxylic acid.

Also according to the present invention we provide a process for the manufacture of said new polyamides which comprises heating the polyamide-forming composition of the kind described above at least until filaments formed from a melt of the polyamide can be extended by cold-drawing into fibres.

Amide-forming derivatives of the ingredients include esters or the amides of the acids, and the pre-formed salts of the acids with the diamines. It is preferred to use the ingredients in the form of the pre-formed salts thereof, since these salts are easily obtained in a pure form and since they contain the respective ingredients in essentially equimolecular proportions. With bis-hexamethylene triamine and adipic acid, however, the salt is not easily isolated and may therefore be used in aqueous solution.

A small proportion of a mono-functional amide-forming reactant, for example acetic acid, may also be used for the purpose of stopping the polyamide-forming reaction at any desired stage in the manner described in Specification No. 495,790.

A small proportion of a delustrant, pigment or other colouring material, for example, titanium dioxide, may be included among the ingredients, or added at any stage in the process.

The amount of bis-hexamethylene triamine that is used as such or in the form of an amide-forming derivative, is necessarily small since the use of a large amount results in the production of an intractable material, insoluble in the normal polyamide solvents and which is unsuitable for moulding. In general, the amount used is from 0.3 to 3.18 molar per cent of the total diamine and aminocarboxylic acid content of the polyamide-forming composition. If less than 0.3% is used the effect on the properties of the polyamide is still

apparent but is so diminished as not to be of technical value. Within this broad range, variations need to be made according to the amount of mono-functional amide-forming reactant used. Thus in absence of such a reactant the preferred molar per cent is from 0.3 to 1.05. With the use of 0.5 molar per cent of acetic acid calculated on the total diamine and aminocarboxylic acid content, the preferred molar per cent of bis-hexamethylene triamine is from 0.6 to 1.8; with 1.4 molar per cent of acetic acid it is 1.2 to 3.18. More than 1.4 molar per cent of acetic acid is not generally used. The preferred proportions to correspond with any desired proportions of monofunctional reactant can be readily determined by trial. The preferred proportions of bis-hexamethylene triamine can be reduced, also, by subjecting the polyamide during manufacture to vacuum treatment or by passing an inert gas through the melt, as is illustrated in the Examples.

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after for  $1\frac{1}{2}$  hours at  $282^{\circ}\text{C}$ . at atmospheric pressure, whilst a slow stream of oxygen-free nitrogen is passed through the melt. The vessel and contents are allowed to cool when the product is obtained as a tough, white solid of inherent viscosity (1% solution in *m*-cresol) 1.09.

#### EXAMPLE 2.

A mixture of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and adipic acid and 0.75 part of the neutral salt formed in aqueous solution from bis-hexamethylene triamine and adipic acid is formed into a polymer in the manner of Example 1 except that the heating at atmospheric pressure is for 20 minutes instead of  $1\frac{1}{2}$  hours. The product is a tough, white solid, inherent viscosity (1% in *m*-cresol) 1.2.

#### EXAMPLE 3.

A solution of 100 parts of the salt formed from equimolecular quantities of hexamethylene diamine and 4 parts of the neutral salt of bis-hexamethylene triamine and adipic acid in 66 parts of distilled water, together with 0.23 part of acetic acid is heated for 1.5 hours at 250 lbs. per square inch pressure in a vessel which has been purged out with oxygen-free nitrogen, the temperature being raised during this period from  $215^{\circ}\text{C}$ . to  $240^{\circ}\text{C}$ . The pressure is gradually reduced over a further  $1\frac{1}{2}$  hours to atmospheric pressure at which pressure the melt temperature is maintained for 1 hour.

The polymer is extruded from the vessel under 30 lb./sq. inch of oxygen-free nitrogen and quenched. The product is a tough, white solid which has a softening point of  $268^{\circ}\text{C}$ . The polyamide is not completely soluble in the solvents used for the determination of intrinsic viscosity.

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The apparatus consists of a cylinder of  $\frac{3}{8}$ " diameter, 4" in length, fitted at the base with a die, the hole of the die being 0.052" in diameter. The cylinder is surrounded by a heating element, lagged to prevent heat loss and means for adjusting and recording the temperature. Fitting into the cylinder is a piston at the upper extremity of which there is a weight of  $12\frac{1}{2}$  lbs.

In carrying out the tests, a quantity of the polyamide is dried at  $110^{\circ}\text{C}$ . for 4 hours in a stream of oxygen-free nitrogen at a pressure of 2 mms. of mercury and is then placed in the cylinder, the temperature of the cylinder is brought up to a temperature just above the softening point of the polyamide, and the temperature is maintained for 10 minutes. The piston is then placed in the cylinder, whereupon the softened polyamide is forced through the hole in the die by virtue of the pressure exerted upon the uppermost surface of the polyamide.

Thereafter, the temperature is increased slowly, and at a series of increasing temperatures, measurements are made of the quantities of molten polyamide extracted from the hole in the die. A record is made of the lowest temperature at which extrusion commences and the lowest temperature at which the polyamide under test is extruded from the hole at the rate of 0.5 gram per minute.

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